

#2
PCT/EP 03 / 0 4 3 0 6

EPO - DG 1

01 07. 2003

(72)



REC'D 24 JUL 2003

WIPO PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten internationalen Patentanmeldung überein.

The attached documents are exact copies of the international patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet international spécifiée à la page suivante.

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

Den Haag, den
The Hague,
La Haye, le

72.06.03

Der Präsident des Europäischen Patentamts
Im Auftrag
For the President of the European Patent Office
Le Président de l'Office européen des brevets
p.o.

NATHALIE KUIPER

Patentanmeldung Nr.
Patent application no.
Demande de brevet n°

PCT/EP 02/11483

BEST AVAILABLE COPY

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation



Meldung Nr.:
Application no.:
Mande n°:

PCT/EP 02/11483

Melder:
Applicant(s):
Mandeur(s):

1. Henkel Kommanditgesellschaft auf Aktien - Düsseldorf, Germany
2. GIORDANI, Paolo - Crema, Italy (US only)
3. RIGAMONTI, Mauro - Opera, Italy (US only)

Zeichnung der Erfindung:

Figure of the invention:

Dessin de l'invention:

Brightening/Passivating Solution and Process for Stainless Steel

Meldetag:

Date of filing:

Date de dépôt:

15 October 2002 (15.10.2002)

Anspruch genommene Priorität(en)

Priority(ies) claimed

Préité(s) revendiquée(s)

at:

te:

ys:

Tag:

Date:

Date:

Aktenzeichen:

File no.

Numéro de dépôt:

Nennung von Vertragsstaaten : Siehe Formblatt PCT/RO/101 (beigefügt)

Designation of contracting states : See Form PCT/RO/101 (enclosed)

Désignation d'états contractants : Voir Formulaire PCT/RO/101 (ci-joint)

Bemerkungen:

Remarks:

Remarques:

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☐ **AP** ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ **EA** Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP** European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA** OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|--|--|
| <input type="checkbox"/> AE United Arab Emirates | <input type="checkbox"/> LC Saint Lucia |
| <input type="checkbox"/> AG Antigua and Barbuda | <input type="checkbox"/> LK Sri Lanka |
| <input type="checkbox"/> AL Albania | <input type="checkbox"/> LR Liberia |
| <input type="checkbox"/> AM Armenia | <input type="checkbox"/> LS Lesotho |
| <input type="checkbox"/> AT Austria | <input type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AU Australia | <input type="checkbox"/> LU Luxembourg |
| <input type="checkbox"/> AZ Azerbaijan | <input type="checkbox"/> LV Latvia |
| <input type="checkbox"/> BA Bosnia and Herzegovina | <input type="checkbox"/> MA Morocco |
| <input type="checkbox"/> BB Barbados | <input type="checkbox"/> MD Republic of Moldova |
| <input type="checkbox"/> BG Bulgaria | <input type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BR Brazil | <input type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BY Belarus | <input type="checkbox"/> MN Mongolia |
| <input type="checkbox"/> BZ Belize | <input type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input type="checkbox"/> MZ Mozambique |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NO Norway |
| <input type="checkbox"/> CR Costa Rica | <input checked="" type="checkbox"/> NZ New Zealand |
| <input type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PL Poland |
| <input type="checkbox"/> CZ Czech Republic | <input type="checkbox"/> PT Portugal |
| <input type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RO Romania |
| <input type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> RU Russian Federation |
| <input type="checkbox"/> DM Dominica | <input type="checkbox"/> SD Sudan |
| <input type="checkbox"/> DZ Algeria | <input type="checkbox"/> SE Sweden |
| <input type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SG Singapore |
| <input type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SI Slovenia |
| <input type="checkbox"/> FI Finland | <input type="checkbox"/> SK Slovakia |
| <input type="checkbox"/> GB United Kingdom | <input type="checkbox"/> SL Sierra Leone |
| <input type="checkbox"/> GD Grenada | <input type="checkbox"/> TJ Tajikistan |
| <input type="checkbox"/> GE Georgia | <input type="checkbox"/> TM Turkmenistan |
| <input type="checkbox"/> GH Ghana | <input type="checkbox"/> TR Turkey |
| <input type="checkbox"/> GM Gambia | <input type="checkbox"/> TT Trinidad and Tobago |
| <input type="checkbox"/> HR Croatia | <input type="checkbox"/> TZ United Republic of Tanzania |
| <input type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> UA Ukraine |
| <input type="checkbox"/> ID Indonesia | <input type="checkbox"/> UG Uganda |
| <input type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> US United States of America |
| <input type="checkbox"/> IN India | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> VN Viet Nam |
| <input type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> ZA South Africa |
| <input type="checkbox"/> KG Kyrgyzstan | <input type="checkbox"/> ZW Zimbabwe |
| <input type="checkbox"/> KP Democratic People's Republic of Korea | Check-box reserved for designating States which have become party to the PCT after issuance of this sheet: |
| <input type="checkbox"/> KR Republic of Korea | <input checked="" type="checkbox"/> PH Philippines |
| <input type="checkbox"/> KZ Kazakhstan | |

Cautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Brightening/Passivating Solution and Process for Stainless Steel

This invention relates to a process for brightening and/or passivating special steel (also termed "stainless steel") after pickling. In general, technical steels are termed non-rusting or stainless if rust formation is prevented under normal environmental conditions, for example in the presence of atmospheric oxygen and moisture and in aqueous solutions. Most high-alloy, so-called corrosion-resistant or acid-resistant steels withstand relatively severe corrosion conditions, for example acids and salt solutions. These steels are generically referred to as special steels. A list of the technically most important special steels, together with the material numbers, identifications and alloy components, as well as the mechanical and chemical properties thereof are given in Ullmanns Encyklopädie der technischen Chemie, 4th Edition, Vol. 22, pp. 106-112 and in German Industrial Standard DIN 17440, July 1985. Special steels are iron based alloys containing at least 10% chromium. The formation of chromium oxide on the material surface imparts to the special steels the corrosion-resistant character thereof.

Special steels may be sub-divided into the following families: austenitic steels, ferritic steels, martensitic steels, precipitation hardened steels and duplex steels. These groups differ in the physical and mechanical properties thereof, as well as in corrosion resistance, as a result of the various alloying constituents. Austenitic special steels are listed as special steels of the 200 and 300 Series. They are the most widely employed special steels and represent 65 to 85% of the special steel market. They are chemically characterized by a chromium content of $> 17\%$ and a nickel content of $> 8\%$. They have a cubic face-centered structure and are outstandingly ductile and weldable. The most widely used of these steels is probably Type UNS S 30400 (Type 304), or "18/8". Modifications include S 32100 (stabilized with titanium) and S 34700 (stabilized with niobium). Alloys having higher contents of chromium, nickel or molybdenum are available and provide increased corrosion resistance. Examples are S 31600, S 31700, S 30900 and S 31000. The 200 Series of austenitic special steels has, on the other hand, a reduced nickel content and contains manganese instead.

When special steel is annealed, hot rolled, etc., a layer of scale forms on the surface, which destroys the desired shiny metallic appearance of the steel surface. This surface layer must therefore be removed after this production step. This removal may be effected by a pickling process according to the state of the art. The oxide-containing surface layer to be removed differs fundamentally from the oxide layer on low-alloy steels or on carbon steels. Apart from iron oxides, the surface layer contains oxides of the alloying elements, for example chromium, nickel, aluminum, titanium or niobium. Particularly in hot rolling, there is an accumulation of chromium oxide in the surface layer. The oxide layer is accordingly enriched with chromium rather than iron. Conversely, this means that the steel layer immediately underneath the oxide layer is depleted in chromium. A pickling process using suitable acidic pickling solutions preferentially dissolves this chromium-depleted layer underneath the oxide layer, with the result that the oxide layer is removed.

Pickling processes for special steel are well-known in the art. Earlier processes use nitric acid-containing pickling baths. These often additionally contain hydrofluoric acid, which on account of its complexing action with respect to iron ions promotes the pickling process. Although such pickling baths are economically efficient and technically satisfactory, they have the serious ecological disadvantage that they emit considerable amounts of nitrogen oxides and release large amounts of nitrates into the waste water.

Intensive efforts have therefore been made in the art to find alternative pickling and passivating processes that do not use nitric acid. Fe(III) ions are a possible substitute for the oxidizing action of nitric acid. The concentration of Fe(III) ions is maintained by hydrogen peroxide, which is added continuously or batch wise to the treatment baths. Such pickling or passivating baths contain about 15 to about 65 g/l of trivalent iron ions. During the pickling process, trivalent iron ions are converted to the divalent form. At the same time, further divalent iron ions are dissolved out from the pickled surface. The pickling bath is thereby depleted in trivalent iron ions during the operation, while divalent iron ions accumulate. The redox potential of the treatment solution is thereby displaced, with the result that the solution finally loses its pickling action. Divalent iron ions are oxidized back to the trivalent state by the continuous or batch wise addition of oxidizing agents, for example hydrogen peroxide, or other oxidizing agents, such as perborates, peracids or also

organic peroxides. In this way, the redox potential necessary for the pickling or passivating action is maintained.

EP-B-505 606 describes a nitric acid-free process for the pickling and passivation of stainless steel, in which the material to be treated is immersed in a bath at a temperature of between 30 and 70 °C and which contains, at least at the beginning of the pickling process, at least 150 g/l of sulfuric acid, at least 15 g/l of Fe(III) ions, and at least 40 g/l HF. This bath furthermore contains up to about 1 g/l of additives, such as non-ionic surfactants and pickling inhibitors. Hydrogen peroxide is added continuously or batch wise to the bath in such amounts that the redox potential remains in the desired range. The other bath constituents are also replenished so that the concentration thereof remains within the optimum operating range. The pickling bath is agitated by blowing in air. Agitation of the pickling bath is necessary in order to achieve a uniform pickling result. A similar process, which differs from the above-described process basically only in the adjusted redox potential, is described in EP-A-582 121.

After the pickling, the surface is chemically activated, which means that, in air, the surface once again becomes coated with an optically interfering surface layer. This may be prevented by passivating the freshly pickled surfaces after or during the pickling. This may be performed in treatment solutions similar to the pickling solutions, a higher redox potential being used for the passivation than for the pickling process. This special passivation step forms an optically invisible passivation layer on the metal surface, and the steel surface thereby preserves its shiny metallic appearance. Whether a treatment solution behaves in a pickling or passivating manner with respect to special steel depends mainly on the established redox potential. Acidic solutions having pH values below about 2.5 have a pickling action if, on account of the presence of oxidizing agents, they have a redox potential in the range from about 200 to about 350 mV with respect to a silver/silver chloride electrode. If the redox potential is raised to values above about 300 to 350 mV, depending on the type of the stainless steel, the treatment solution has a passivating effect. In case of less noble materials (ferritic, martensitic grades) this inferior limit will shift to higher values.

During the pickling of stainless steel, in particular during the pickling of ferritic and martensitic stainless steel, but also during the pickling of austenitic stainless steel containing sulfur in the alloy, a gray black smut is formed during the pickling itself. This is due to the formation of by-products on the surface due to the pickling reaction. In particular ferritic and martensitic grades must be passivated after the pickling using high oxidizing chemical solutions in a separate step. This step provides both the bleaching of the material and the passivation of the surface.

The traditional solution used according to the state of the art is a solution formed by nitric acid at a concentration ranging from 6% to 20%, which may optionally contain small amounts of hydrofluoric acid (generally from 1 to 10 g/l). The possible requirement of the presence of HF is due to the fact that some ferritic and martensitic stainless steel grades need a light etching of the surface to allow an efficient bleaching of the surface itself. This means that two different solutions are necessary in practice, one containing HF to solve the problem described above, and another one free of HF, due to the fact that the presence of HF may increase too much the reaction rate on the base alloy, shifting the behaviour of the solution from passivation to etching. This would cause high metal dissolution of the base alloy and a further darkening of the surface.

Furthermore, due to the very low HF concentration used, the traditional system is extremely difficult to be controlled and replenished in a proper manner.

In recent years nitric acid free pickling processes were successfully applied in the stainless steel industry in order to solve the ecological problems caused by the presence of nitric acid. One of the remaining open problems for the complete removal of HNO_3 from the industrial plant was just the substitution of nitric acid in the passivation step. The problem solutions proposed were substantially based on acid solutions containing hydrogen peroxide as the oxidizing agent. However, the performance of these solution showed to be constantly inferior to the nitric acid containing solutions for two fundamental reasons:

The low stability of hydrogen peroxide during the use due to the destroying effect of the metal ions slowly dissolved from the outer surface during the process;

The poorer surface finishing quality of the ferritic/martensitic grades compared to the HNO_3 based solutions.

Possible solutions exist to solve problem a) (see, e.g., WO 01/49899 and GB 1,449,525), enabling hydrogen peroxide based solutions to tolerate iron ion concentrations as high as 10-15 g/l without destroying the excess of hydrogen peroxide necessary to get passivation. However, it is clear that a suitable industrial problem solution requires to have both problem a) and b) solved at the same time.

This difficulty is increased by the fact that in any case, when using nitric acid free passivation solutions for ferritic and martensitic grades, for many grades there always exists the need to add some HF to allow the bleaching of the surface, as for HNO_3 containing solutions. The addition of HF has the drawback to dissolve much more iron from the substrate, decreasing at the same time the shelf life of the hydrogen peroxide based passivation solution. In any case the surface quality obtained is normally lower than using HNO_3 based solutions.

Therefore, there is a need for a bleaching and/or passivating process, for ecological reasons preferably free from nitric acid, which can be used for various types of stainless steel without changing the composition of the process solution, and without the risk to re-etch the surface.

The invention is based on the discovery that the replacement of HF by complex fluoride ions of elements of groups 4, 13, or 14 (old notation: groups IVa, III, or IV, i.e. the groups beginning with the elements Ti, B, or C, respectively) of the periodic table of the chemical elements can solve the problems described above.

In a most general aspect, the subject matter of the present invention is the use of complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements in concentrations from 30, preferably from 65, mmols per liter to 300, preferably to 220, millimoles per liter in process solutions for bleaching and/or passivating pickled surfaces of stainless steel.

These process solutions preferably contain one or more strong acids (equally strong or stronger than phosphoric acid) in order to have a pH-value not higher than 2.5, preferably not higher than 1. This ensures high bleaching power of the process solution. Additionally, the strong acids keep the ionic strength of the solution approximately constant.

Concentrations of the strong acids in the range of 2 to 100 g/l (as the total of the strong acids) are usually sufficient. The strong acids may, for example, be selected from nitric acid, phosphoric acid, hydrochloric acid, and sulfuric acid. Hydrochloric acid is less preferred, because it might lead to chloride pitting. For the ecological reasons referred to above it is preferred that strong acids different from nitric acid are used. However, even if nitric acid is used, the present invention leads to the practical advantage that only one bleaching solution can be used for all grades of stainless steel without the risk of over-etching the surface, instead of having to work with at least two different solutions (one free from HF, one containing HF), depending on the material to be bleached/passivated.

In addition, the process solution contains an oxidizing agent which ensures that the surface of the pickled stainless steel is brought into the passivated state. Possible oxidizing agents (which may be defined in the present case as agents which have an oxidizing power sufficient to oxidize Fe(II) ions to Fe(III) ions in acidic aqueous solutions) are: ferric ions themselves, permanganate ions, anions of oxoacids of halogen atoms like chlorates or perchlorates (even if less preferred due to possible chloride pitting), or compounds containing peroxo groups like perborates, persulfuric acid, peroxodisulfuric acid, peroxides, or, most preferred for ecological reasons, H_2O_2 . In all embodiments of the present invention, the oxidizing agent is preferably present in a concentration, expressed as the equivalent concentration of H_2O_2 , in a range from about 1, preferably from about 4, to about 30, preferably to about 20 g/l, calculated as undiluted H_2O_2 . „Equivalent concentration of H_2O_2 “ means the concentration absorbing the same number of electrons in the redox reaction. These explanations of strong acids and oxidizing agents hold for all embodiments of the present invention, described above or below.

If H_2O_2 or compounds yielding H_2O_2 in the process solution are used as the oxidizing agent, the process solution preferably also comprises a hydrogen peroxide stabilizer (referred to as component d) in claims 4 and 7) in order to prevent excessive decomposition of hydrogen peroxide caused by the catalytic action of transition metal ions

in the process solution. If an efficient stabilizer is chosen, Fe(III) concentrations in the process solution as high as 10 to 15 g/l are tolerated without causing excessive decomposition of hydrogen peroxide. Suitable stabilizers are known in the state of the art. For example, EP-A-582 121 discloses 8-hydroxyquinoline, sodium stearate, phosphoric acid, salicylic acid, pyridine carboxylic acid, and especially phenacetine as efficient stabilizers. Especially preferred stabilizers are glycole ethers, as taught in GB 1,449,525, especially in combination with phosphoric acid, as disclosed in WO 01/49899. Therefore, even if phosphoric acid is not chosen as a strong acid in component a), some phosphoric acid is preferably added as part of the stabilizer package.

In any aspect of the present invention, the complex fluorides of elements of groups 4, 13, or 14 of the periodic table of the chemical elements can be added as free acids or as salts, preferably alkaline metal salts, which are soluble in the process solution at least in an amount to result in the indicated concentration of complex fluoride ions. In any case an equilibrium state between the acid and the salt form of the complex fluoride ions will be established, depending on the pH value of the process solution and the dissociation constant of the complex fluoride acid. For reasons of availability, the complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements are preferably selected from complex fluoride ions (in salt or acid form) of the elements B, Si, Ti, and Zr. Special examples are BF_4^- , SiF_6^{2-} , TiF_6^{2-} , and ZrF_6^{2-} , either in the form of the corresponding acids or of their salts. For economic and ecological reasons, SiF_6^{2-} is especially preferred.

In a more special aspect, the subject matter of the present invention is a process solution for bleaching and/or passivating pickled surfaces of stainless steel comprising:

- a) one or more strong acids as explained above, preferably, but not necessarily different from nitric acid.
- b) one or more oxidizing agents as outlined above,
- c) complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements as outlined above in concentrations from 50, preferably from 65 mmol/l to 300, preferably to 220 mmol per liter.

As outlined above, also in this more special aspect of the present invention

- a) the strong acid is present in a concentration from 2 to 100 g/l, and
- b) the oxidizing agent is present in a concentration, expressed as the equivalent concentration of H_2O_2 , in the range from about 1, preferably from about 4, to about 30, preferably to about 20 g/l.

In a further aspect the present invention comprises a replenisher solution for a process solution described above, comprising

- a) one or more strong acids preferably, but not necessarily different from nitric acid,
- b) one or more oxidizing agents,
- c) complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements

in concentrations higher than those defined in claims 3 and 5

Also in this aspect of the invention, components a), b), and c) are preferably selected according to the explanations above. This aspect of the invention accounts for the fact that these three components are consumed during the brightening/passivation reaction.

Differences in the consumption rate, which can be detected by analysis of the process solution at different times, can be accounted for by formulating a replenisher solution in which the three components a), b), and c) are present in a mass ratio different from their ratio in the process solution itself. The stabilizer for hydrogen peroxide, however, is either not consumed at all, or in a much lesser amount. Therefore, the stabilizer needs not be replenished in a similar amount as the other components a), b), and c). Thus, the process solution is replenished in the most efficient and economic way.

On the other hand, if there is a strong consumption of the oxidizing agent compared to the other ingredients of the process solution, it might be advantageous to feed the oxidizing agent, especially hydrogen peroxide or a compound yielding hydrogen peroxide in the process solution, independently from the other components. In this case, it is preferred to use an additive solution for a process solution as described above, comprising

- a) one or more strong acids preferably, but not necessarily different from nitric acid,
- c) complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements,

d) a hydrogen peroxide stabilizer
in concentrations higher than those defined in claims 3 and 5.

This additive solution is yet another aspect of the present invention. Of course, the explanations given above for preferred components a), c), and d) are valid for this aspect of the invention as well. Mass ratios of components a), c), and d) in the additive solutions may be chosen according to the experimentally determined consumption rates of these components in the process solution.

Finally, the present invention comprises a process for brightening and/or passivating of pickled surfaces of stainless steel, wherein the surfaces are brought into contact (by dip or spray processes) with a process solution according to one or more of claims 3 to 7, described in more detail above. In dip process the solution is preferably agitated by the injection of air or by mechanical agitation means. The process solution may have a temperature in the range from 15 to 40 °C, preferably at most 30 °C. The contact time depends on the type of stainless steel and on the kind of pickling treatment prior to the bleaching/passivating step. Usual contact times will be in the range from 10 seconds (for strip) to 10 minutes. The contact is terminated by rinsing the stainless steel surface with water, preferably in a power spray process, spraying water with elevated pressure onto the stainless steel surface.

It should be evident from the description above that the process according to the present invention is part of the treatment chain: pretreatment (acid treatment, molten salt treatment, shot peening, mechanical cracking of the scale, and the like), pickling (in one ore more steps, e.g. using pickling solutions as quoted in the introductory part), bleaching/passivating according to the present invention, water rinse, and drying.

The invention can be applied to the production of stainless steel, especially ferritic or martensitic grades, in any form, such as wire, rod, tube, plate, coil, and finished articles. It is possible to use a single process solution for all grades of ferritic and martensitic stainless steel, without the requirement to adjust the composition of the process solution to the grade of the stainless steel treated. The same solution can be used for removing smuts after pickling from the surface of austenitic grades containing sulfur (e.g. AISI 303). Compared

to the state of the art of nitric acid free bleaching solutions, the process solution according to the present invention dissolves a smaller amount of alloy in order to get the necessary smut removal. This generates less waste, increases the speed, improves the surface finishing, and reduces the decomposition rate of hydrogen peroxide. Thus, the ecological and/or economic disadvantages of using HNO_3 -based bleaching/passivating solutions can be avoided without any drawbacks or even with advantages in surface finishing or in process economy (e.g. waste generated, treatment time). And even if nitric acid is used as the strong acid, the present invention leads to the practical advantage that only one bleaching solution can be used for all grades of stainless steel without the risk of over-etching the surface, instead of having to work with at least two different solutions (one free from HF, one containing HF), depending on the material to be bleached/passivated.

Examples

Examples series 1

AISI 420 F is one of the most critical grades according to the aim of the invention, due to the very high reactivity and due to moving in a quite complicated manner from the passivity to the activity regime (probably into the transpassivity regime using HNO_3).

Wire samples of hot rolled AISI 420 F were pre-treated with reduction molten salts and then pickled for 10 minutes in sulfuric acid solution and for 10 minutes in a Cleanox[®] solution (commercialized pickling process of the applicant according to EP-B-582 121, based on $\text{H}_2\text{SO}_4/\text{HF}/\text{Fe(III)}$, wherein the Fe(III) concentration and hence the redox potential is managed by the addition of hydrogen peroxide).

After rising the samples were completely dark due to the presence of black smut on the surface. The samples were weighted and then immediately brightened and passivated in different solutions for a time of 4 minutes at room temperature (25°C) according to the state of the art (both nitric acid based or nitric acid free: comparative examples) and to the invention. After this step the samples were rinsed with a low pressure water spray for 1

minute, dried and weighted again. At the end the samples were evaluated visually to compare the surface brightness according to an arbitrary scale ranging from 1 to 5, where :

- 1 = very bad (similar to the appearance before brightening)
- 2 = bad (surface partially bleached; darkening of a white paper rubbed on the surface)
- 3 = acceptable (quite bleached surface but still some residuals after white paper rubbing)
- 4 = good (practically no black residuals passing paper on the surface, but not very homogeneous)
- 5 = very good (completely bleached and homogeneous surface; no black residuals when rubbing the surface with the paper).

Table 1: Bleaching results

Identification (comp. = comparative, inv. = invention)	Composition	Concen- tration (g/l)	Weight loss (g/m ²)	Surface Brightness
1a (comp.)	HNO ₃	100	28	4
2a (comp.)	HNO ₃ /HF	100/2	125	3
1b (comp.)	H ₂ SO ₄ /H ₂ O ₂	20/6	1,8	2
2b (comp.)	H ₂ SO ₄ /H ₂ O ₂	80/6	1,9	3
3b (comp.)	H ₂ SO ₄ /H ₂ O ₂	20/80	0,9	2
1c (comp.)	H ₂ SO ₄ /H ₂ O ₂ /HF	20/6/2	111	2
2c (comp.)	H ₂ SO ₄ /H ₂ O ₂ /HF	80/6/2	100	2
3c (comp.)	H ₂ SO ₄ /H ₂ O ₂ /HF	20/24/2	70	4
4c (comp.)	H ₂ SO ₄ /H ₂ O ₂ /HF	80/24/2	70	4
1d (comp.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	0/6/20	1,0	2
2d (comp.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	10/6/5	2,3	2
3d (comp.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	20/6/5	1,5	2
4d (inv.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	10/6/10	26,0	4
5d (inv.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	5/6/20	27,1	5
6d (inv.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	20/6/10	26,2	5
7d (inv.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	20/6/15	26,5	5
8d (inv.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	20/6/20	35,7	5
1e (comp.)	H ₃ PO ₄ /H ₂ O ₂ /H ₂ SiF ₆	30/6/8	1,5	2
2e (inv.)	H ₃ PO ₄ /H ₂ O ₂ /H ₂ SiF ₆	30/6/15	17,4	5
3e (inv.)	H ₃ PO ₄ /H ₂ O ₂ /H ₂ SiF ₆	30/6/20	20,4	5

It is quite clear from the data in table 1 that the removal of the black smut covering the surface to get a clear and bright surface is strictly joined to a minimum weight loss during the operation (in this case 15 – 27 g/m²). These data are comparable with the data obtained for HNO₃ solution.

The addition of HF to HNO₃ or the H₂SO₄/H₂O₂ system also at very low concentration generates immediately a re-etching of the base alloy with the tendency to generate again a gray-black surface, if one does not increase considerably the oxidizing agent concentration in the case of the H₂SO₄/H₂O₂ system. But this results in weight losses much higher than the reference (HNO₃), and thus in considerable costs due to consumption of hydrogen peroxide.

It is a clear advantage of adding fluoride complexes that one can work in a well manageable concentration range without causing the re-etching of the surface.

Examples series 2.

Another martensitic grade (AISI 410) was bleached after pickling to confirm the data obtained on the previous most difficult grade. The process sequence was the same as for example series 1.

Table 2: Bleaching results

Identification (comp. = comparative, inv. = invention)	Composition	AISI 410		
		Concen- tration (g/l)	Weight loss (g/m ²)	Surface Brightness
1a(comp.)	HNO ₃	100	1,0	4
2a(comp.)	HNO ₃ /HF	100/2	10,5	5
1b(comp.)	H ₂ SO ₄ /H ₂ O ₂	20/6	0,5	3
2b(comp.)	H ₂ SO ₄ /H ₂ O ₂	20/20	0,3	3
3b(comp.)	H ₂ SO ₄ /H ₂ O ₂	50/6	0,3	3
1c(comp.)	H ₂ SO ₄ /H ₂ O ₂ /HF	20/6/2	11	5
2c(comp.)	H ₂ SO ₄ /H ₂ O ₂ /HF	20/20/2	9,7	5
1d(inv.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	20/6/15	5,7	5
2d(inv.)	H ₂ SO ₄ /H ₂ O ₂ /H ₂ SiF ₆	40/20/20	6,3	5
1e(inv.)	H ₃ PO ₄ /H ₂ O ₂ /H ₂ SiF ₆	30/6/15	3,3	5
2e(inv.)	H ₃ PO ₄ /H ₂ O ₂ /H ₂ SiF ₆	30/6/30	5,4	5

This grade of steel is an example where the addition of HF to the HNO₃ solution allows to improve the finishing of the stainless steel surface. As this steel is more corrosion resistant than AISI 420 F, the increase in weight loss is acceptable and does not cause any important re-etching of the base alloy. A similar behaviour is given by the H₂SO₄/H₂O₂/HF solution with also similar weight losses. However, in this case the solution of the invention allows to get the best finishing result for all the combinations tested, but with a weight loss about 50% lower than the state of the art.

Examples series 3: 4xx grades

Comparative behaviour among different complex fluoride acids was tested on two other different martensitic grades (420B, 420C1). Also the behaviour of the addition of fluosilicic acid to HNO_3 was evaluated.

Solutions	1	2	3	4	5	6	7	8
H_2SO_4 g/l			20			20	20	20
HNO_3 g/l	100	100		25	100			
HF g/l		1						
H_2SiF_6 g/l			15	15	15			
H_2TiF_6 g/l						17,1		
H_2ZrF_6 g/l							21,6	
HBF_4 g/l								13,7
H_2O_2 g/l			6			6	6	6

Results

Solution	420B		420C1	
	Weight loss (g/m ²)	Bleaching index	Weight loss (g/m ²)	Bleaching index
1	4,1	4	4,3	5
2	13,8	5	22,6	4
3	11,1	5	20,3	5
4	6,3	4	9,5	4
5	7,8	5	11,1	5
6	24,3	5	30,3	5
7	18,2	5	31,8	5
8	5,1	5	12,4	5

Examples series 4: 3xx grades

One of the reasons to use a brightening solution for austenitic grades is the removal from the surface of possible smut or deposits forming during the pickling step. This can happen more often for the less noble austenitic grades such as the sulphur containing alloys. The surface of these grades at the end of the pickling could be covered by a gray /black smut due to the by-product reactions containing sulphate . In addition it can be possible that also copper, an element normally present in the pickling baths in which copper containing alloys are pickled, deposits on the steel surface forming a red brown film, that must be removed.

The following tests were made with AISI 303 grade wire samples.

Samples of AISI 303 were pickled in the following solutions:

Pickling solutions	CX 1	CX 2
H ₂ SO ₄	100 g/l	100 g/l
HF	30 g/l	30 g/l
Fe ³⁺	20 g/l	20 g/l
Fe ²⁺	30 g/l	30 g/l
Cu ⁺²	-	1,4
Temperature	35°C	35°C

After pickling in solutions CX 1 and CX 2, the samples were brightened for comparison in the brightening solutions A) B), and C) below for a time of 4 minutes.

Brightening solutions	A) HNO ₃	B) HNO ₃ + HF	C) Invention
HNO ₃ g/l	100	100	//
HF g/l	//	10	//
H ₂ SO ₄ g/l	//	//	20
H ₂ O ₂ (100%), g/l	//	//	20
H ₂ SiF ₆ g/l	//	//	20
H ₂ O ₂ Stabilizer *	//	//	7
Temperature	28°C	28°C	28°C

* Mixture 1:1 by weight of phosphoric acid and butylcellosolve^R

After that the samples were rinsed with water by dip followed by a low pressure spray fresh water rinse. On the samples pickled in solution CX1 the weight loss during the brightening step were also measured:

	Weight loss (g/m ²)	Bleaching Index	Copper removal (Yes / No)	
			After Dip rinsing	After spray rinsing
A) HNO ₃	4,2	4	No	Yes
B) HNO ₃ + HF	24,6	5	No	Yes
C) Invention	1,5	5	Yes	Yes

The solution C) according to the invention showed very good brightening properties together with a very low weight loss. In addition the copper removal ability was better than in the traditional solution, being effective also without the final spray rinse.

Claims:

1. The use of complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements in concentrations from 30 to 300 millimoles per liter in process solutions for bleaching and/or passivating pickled surfaces of stainless steel.
2. The use according to claim 1 wherein the process solution contains from 2 to 100 g/l of one or more strong acids.
3. A process solution for bleaching and/or passivating pickled surfaces of stainless steel comprising:
 - a) one or more strong acids,
 - b) one or more oxidizing agents,
 - c) complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements in concentrations from 50 to 300 mmoles per liter.
4. A process solution according to claim 4, wherein the oxidizing agent b) is selected from compounds containing a peroxo-group, and which additionally comprises
 - d) a hydrogen peroxide stabilizer.
5. A process solution according to one or both of claims 3 and 4, wherein
 - a) the strong acid is present in a concentration from 2 to 100 g/l, and
 - b) the oxidizing agent is present in a concentration, expressed as the equivalent concentration of H_2O_2 , in the range from 1 to 30 g/l.
6. A replenisher solution for a process solution according to one or more of claims 3 to 5, comprising
 - a) one or more strong acids,
 - b) one or more oxidizing agents,
 - c) complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements

in concentrations higher than those defined in claims 3 and 5.

7. An additive solution for a process solution according to one or both of claims 4 and 5, comprising
 - a) one or more strong acids,
 - c) complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements,
 - d) a hydrogen peroxide stabilizerin concentrations higher than those defined in claims 3 and 5.
8. The use according to one or both of claims 1 and 2 or the solution according to one or more of claims 3 to 7, wherein the complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements are selected from complex fluoride ions of the elements B, Si, Ti, and Zr.
9. The use according to one or both of claims 1 and 2 or the solution according to one or more of claims 3 to 7, wherein the strong acids are selected from sulfuric acid, phosphoric acid, and hydrochloric acid, or mixtures thereof.
10. A process for brightening and/or passivating of pickled surfaces of stainless steel, wherein the surfaces are brought into contact with a process solution according to one or more of claims 3 to 5.

Abstract

The use of complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements (preferably selected from complex fluoride ions of the elements B, Si, Ti, and Zr) in concentrations from 30 to 300 millimoles per liter in process solutions for bleaching and/or passivating pickled surfaces of stainless steel; a process solution for bleaching and/or passivating pickled surfaces of stainless steel comprising: a) one or more strong acids, b) one or more oxidizing agents, c) complex fluoride ions of elements of groups 4, 13, or 14 of the periodic table of the chemical elements in concentrations from 50 to 300 mmols per liter; replenisher or additive concentrates containing different combinations of active substances thereof; a process for brightening and/or passivating of pickled surfaces of stainless steel, wherein the surfaces are brought into contact with such a process solution.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.